

2. THERMOELECTRIC PROPERTIES OF BORON CARBIDES

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INTRODUCTION

Boron carbides are ceramic materials with unusual properties and applications. These refractory materials ($T_m > 2600\text{K}$) exist as a single phase over a wide range of stoichiometries, from 20 a/o carbon to less than 10 a/o carbon (Bouchacourt and Thevenot 1981). The relatively low density ($\approx 2.5 \text{ g/cm}^3$) and exceptional hardness lead to applications in the area of ceramic armor. In addition, ^{10}B has a large capture cross section for thermal neutrons. This fact, along with the robust nature of the structure in a high radiation environment, leads to the use of boron carbides as nuclear reactor control materials. Because of a combination of unusual high temperature electronic and thermal properties, boron carbides also make efficient very high temperature (p-type) thermoelectrics. In this paper, we shall review the electrical and thermal properties of boron carbides and describe recent progress in understanding these properties.

TRANSPORT PROPERTIES

Electronic transport measurements have been made from 77K to 1200K on hot-pressed boron carbides with composition between B_4C and B_9C (Wood and Emin 1985). The electrical conductivity (σ), shown schematically in Figure 1, is relatively large and thermally-activated. The Hall mobility, also depicted in Figure 1, is low and also thermally-activated.

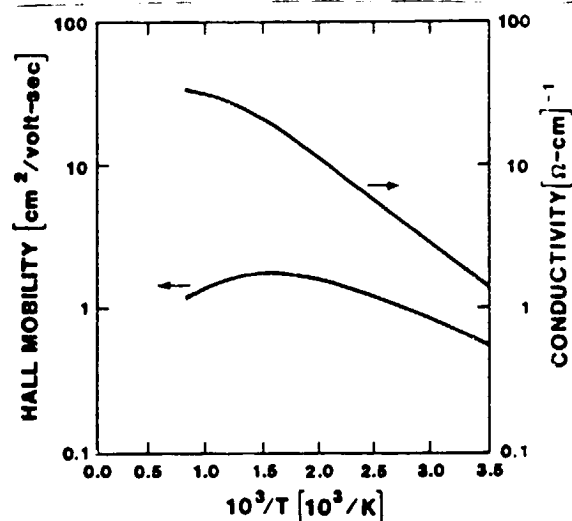


Figure 1. Temperature dependence of the Hall mobility and conductivity characteristic of boron carbides.

These measurements are consistent with the hopping of a large ($\approx 10^{21}/\text{cm}^3$), composition-dependent but temperature-independent density of polaronic holes. A much smaller density of localized spins ($\approx 10^{19}/\text{cm}^3$) (Venturini et al. 1987, Azevedo et al. 1986) suggests that the carriers are spinless singlet bipolarons. Consistent with the nearly-degenerate carrier density, one would expect the Seebeck coefficient (S) to be small and relatively insensitive to temperature changes, as depicted in curve (a) of Figure 2. The experimental results (Wood and Emin 1985), however, show anomalously large p-type Seebeck coefficients that increases

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approximately linearly with temperature, as shown in curve (b) of Figure 2. This anomalous behavior generally arises from inequivalent electron-lattice coupling strengths at the sites involved in hopping transport (Emin 1975). In the boron carbides, this inequivalence is associated with disorder in the structure of the solid.

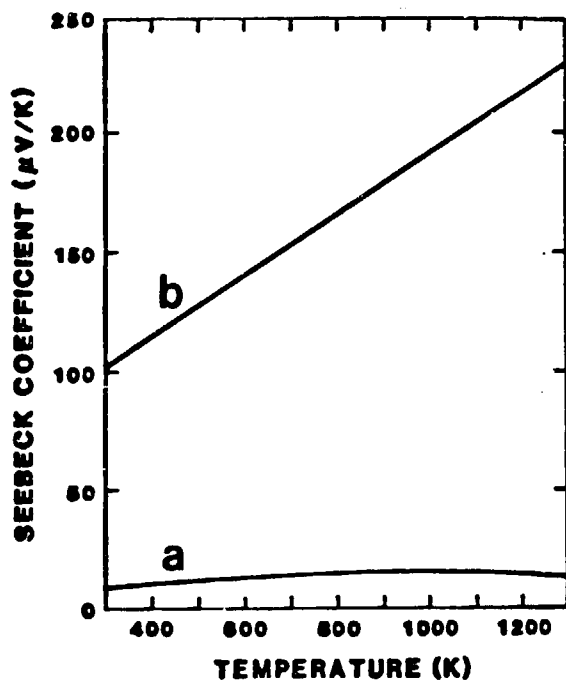


Figure 2. a) Seebeck coefficient vs. temperature for an ordered, nearly-degenerate material. b) Representative experimental Seebeck coefficient for boron carbides.

One would expect, given the extreme hardness and the high speed of sound found in boron carbides, that the boron carbides would be good thermal conductors. The experimentally-observed behavior (Wood et al. 1985), displayed in Figure 3 for a variety of samples, is more complex, however. At B_4C , the thermal conductivity (κ) behaves in the manner typical of crystalline solids, falling with increasing temperature. For compositions with less carbon, however, the thermal conductivity is low and relatively independent of temperature. This behavior is more characteristic of amorphous solids than crystals. Thus, the thermal transport behavior of boron carbide is also anomalous.

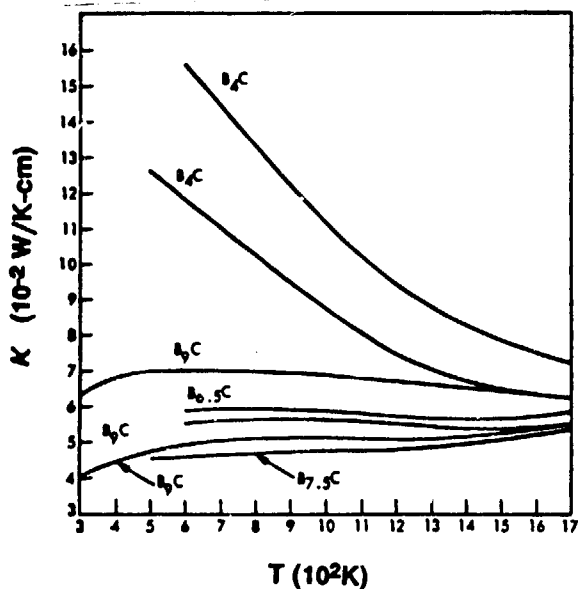


Figure 3. Thermal conductivity vs. temperature for boron carbides of various compositions.

These anomalous transport properties have a large impact on the thermoelectric figure of merit, $Z=S^2\sigma/\kappa$, of boron carbides. The anomalously large Seebeck coefficient and the unexpectedly low thermal conductivity yield a figure of merit that is orders of magnitude larger than would be expected for such solids. In addition, with σ and S increasing with temperature and κ being temperature independent, the thermoelectric properties of boron carbides improve as temperature increases. Thus, boron carbides offer the potential for efficient thermoelectric power conversion at very high temperature. Another potential advantage to the use of boron carbides is the robust nature of the materials in a high radiation environment. Neutron and electron damage studies on the materials indicate that radiation damage is limited. Thus, with ^{11}B enrichment, boron carbides are potentially much less susceptible to radiation damage than other thermoelectric materials.

Further improvement in the properties of boron carbides will require an understanding of the origin of the anomalous transport properties and the unusual radiation effects. A number of questions stand out from the preceding discussion of properties: What is the precise origin of bipolaron formation in boron carbides? What is the source of the disorder leading to the anomalous Seebeck coefficient? Why is the thermal conductivity of boron carbides glasslike at carbon content below B_4C ? How does radiation damage affect the electrical and thermal properties of boron carbides? Why are boron carbides p-type? and, ultimately, Can n-type boron carbides be made? Recent work in our group has addressed such questions.

STRUCTURE AND THEORY

The crystal structure of boron carbides is shown in Figure 4. Boron-rich icosahedra (twelve-atom clusters) are located at the corners of a rhombohedral unit cell, and a three-atom chain bonds the icosahedra together along the long unit cell diagonal. Considerable progress has been made in understanding how the structure changes with composition and the effect of such changes on the properties described above.

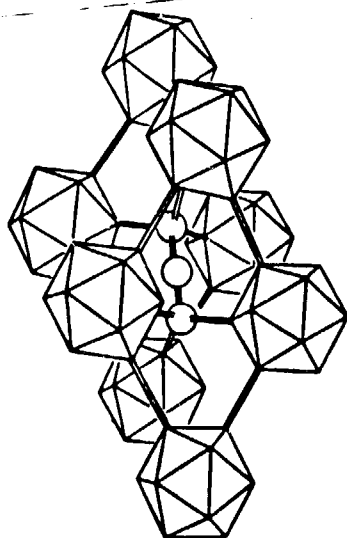


Figure 4. Crystal structure of boron carbides. A boron or a carbon atom is located at each vertex of the icosahedra. The three atom chain lies along the long diagonal of the rhombohedral unit cell.

At B_4C , the structure has been shown to consist primarily of B_{11}C icosahedra linked by CBC chains (Morosin et al. 1986). Theoretical modeling of the system has shown (Emin 1987) that the bipolaronic holes are located on the icosahedral structures. The relatively large size of the icosahedron assists bipolaron formation by reducing Coulombic repulsion between the carriers. P-type conductivity occurs over the entire composition range if the hopping occurs between icosahedra that contain one carbon atom, i.e. B_{11}C icosahedra. Thus, the model of the system that evolves is one in which carbon is removed preferentially from chain sites, with formation of BBC chains, as boron replaces carbon in B_4C . Supporting evidence for this model has recently been provided by a Raman spectroscopic study of boron carbides of various composition (Tallant et al. 1988). The distribution of a single carbon atom among the icosahedral sites also provides substitutional disorder and therefore is a potential source of the inequivalence in the icosahedral hopping sites required for the anomalous Seebeck coefficient. Additionally, hot-pressed boron carbides are notable in having a large density of

twins along the rhombohedral planes of the crystal structure. This feature means that microstructure may also play a role in the inequivalence of hopping sites (Aselage et al. 1987). Recent Seebeck measurements on flux-grown crystals of B_4C , with few to no twin defects, however, are similar to hot pressed materials (Wood 1988). The latter result suggests that the inequivalence in hopping sites is due only to the intrinsic substitutional disorder in boron carbides.

Structural changes with composition also affect the thermal transport in boron carbides. As the carbon concentration is reduced from 20%, CBC chains are progressively replaced by BBC chains. The B-B bonds of the BBC chains are considerably less stiff than the C-B bonds of the CBC and BBC chains. Thus, vibrational inhomogeneities are introduced as BBC chains begin to replace CBC chains. Preliminary theoretical results suggest that this vibrational disorder has the effect of reducing the thermal conductivity of the crystalline solid to that of a glasslike material (Emin et al. 1987).

CONCLUSIONS

Boron carbides are refractory solids with unique electronic and thermal transport properties. The boron carbides are very efficient, very high temperature p-type thermoelectrics. We have made considerable progress in understanding the nature of boron carbides and the origin of the unusual properties. Continued research will provide insight into the nature of radiation effects in the materials and the possibility of creating efficient n-type materials. Preliminary measurements on a low carbon CVD sample ($\approx 90\%$ rhombohedral phase) show n-type behavior at room temperature (Campbell et al. 1987).

Acknowledgments

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